Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Room-Temperature Dielectric Switching in a Host-Guest Crown Ether Inclusion

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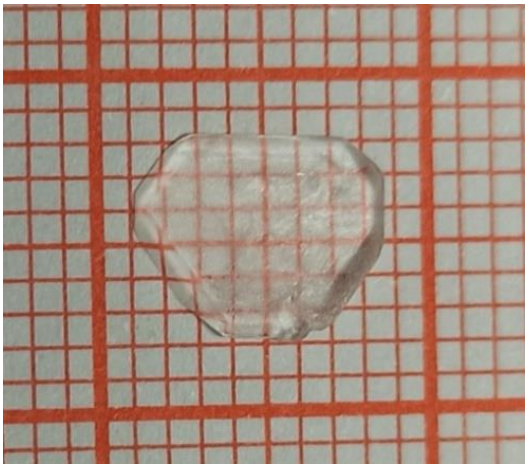

Fig. S1 The crystal sample of **1**.

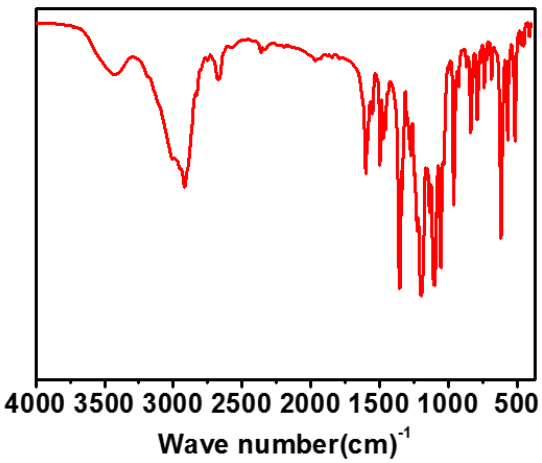

Fig. S2 IR spectrum of **1** at room temperature.

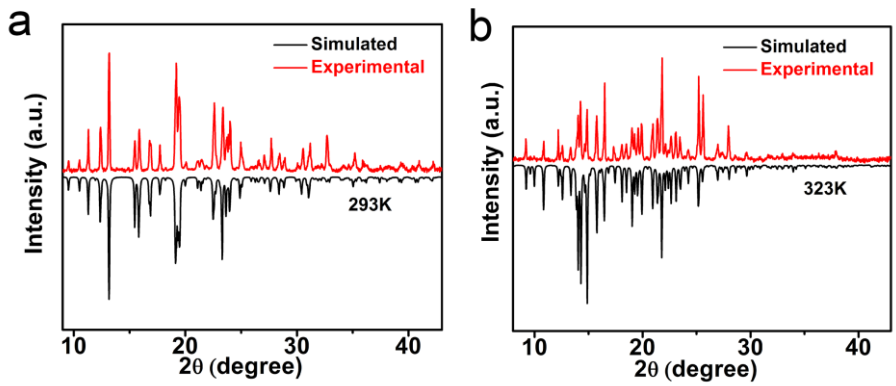

Fig. S3 PXRD pattern of experiments and simulations of **1** at 293 K (a) and 323 K (b), respectively.

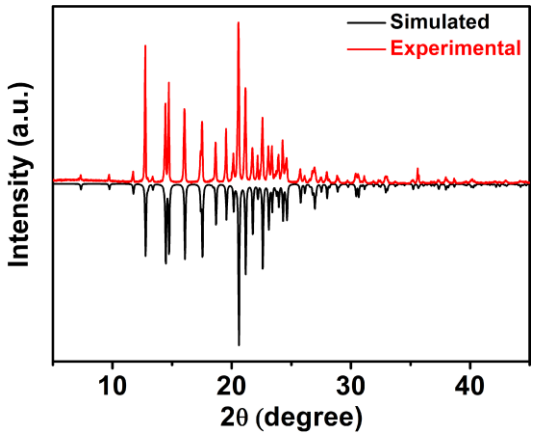

Fig. S4 PXRD pattern of experiments and simulations of [($C_7H_{10}NO$)(18-crown-6)][PF_6] at 293 K (a) and 323 K (b), respectively.

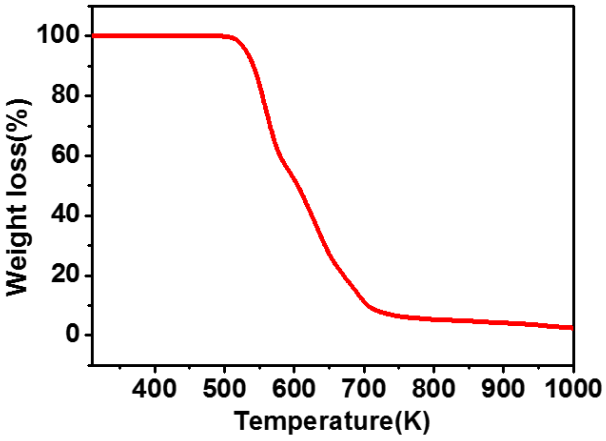

Fig. S5 TGA data for **1**.

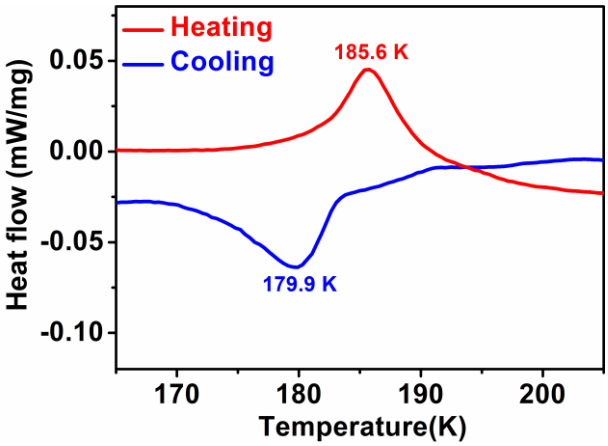

Fig. S6 DSC curve of [($C_7H_{10}NO$)(18-crown-6)][PF_6] measured in a heating–cooling cycle.

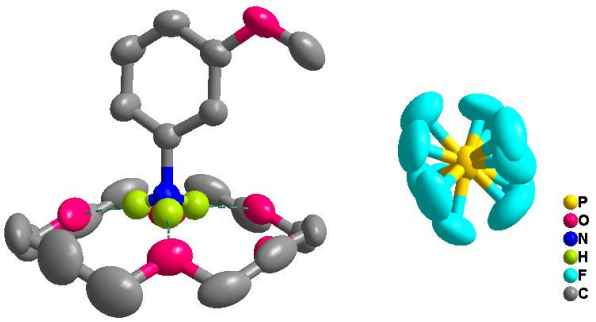

Fig. S7 Molecular structures of [($C_7H_{10}NO$)(18-crown-6)][PF_6] at 293 K. Part of H atoms were omitted for clarity.

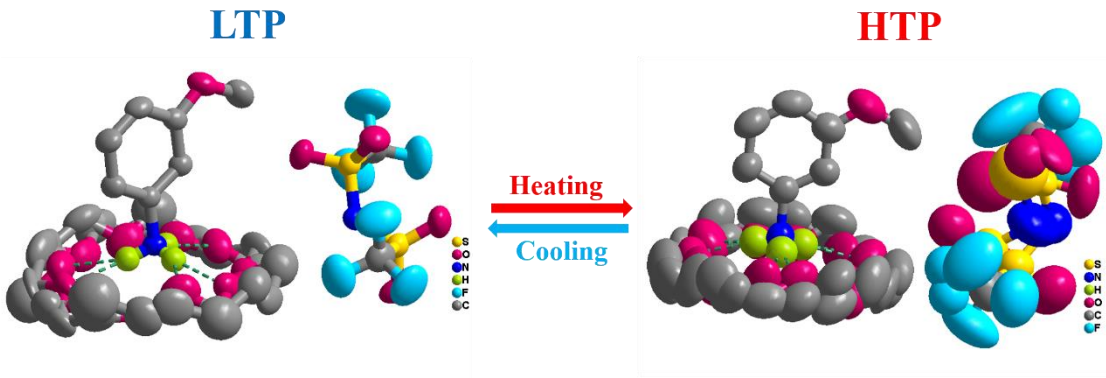

Fig. S8 Molecular structures of **1** at 293 K (in LTP) and 323 K (in HTP). Part of H atoms were omitted for clarity.

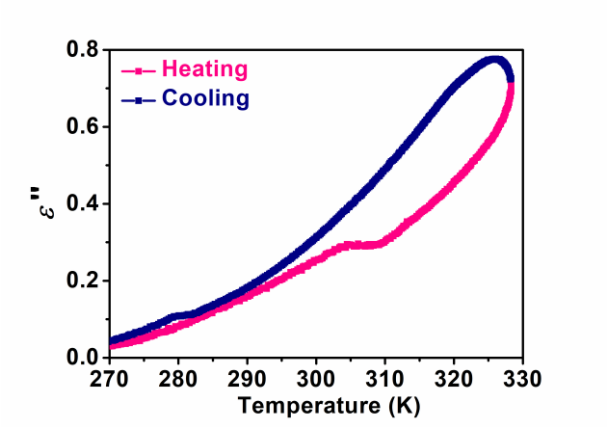

Fig. S9 The dielectric imaginary of **1** measured under 1 MHz in a heating and cooling run.

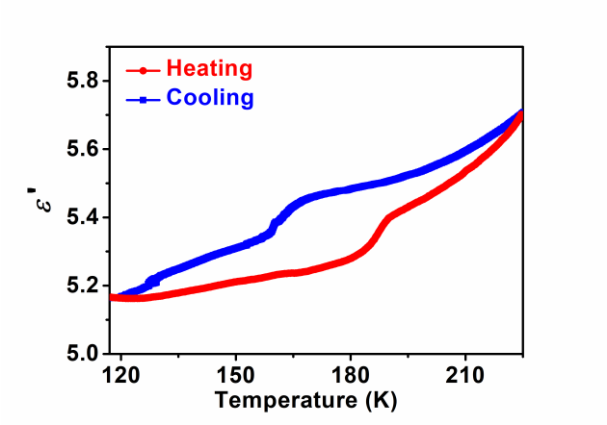

Fig. S10 Temperature-dependence of the real part (ε′) of the polycrystalline sample for [($C_7H_{10}NO$)(18-crown-6)][PF_6] at 1 MHz in a heating and cooling run.

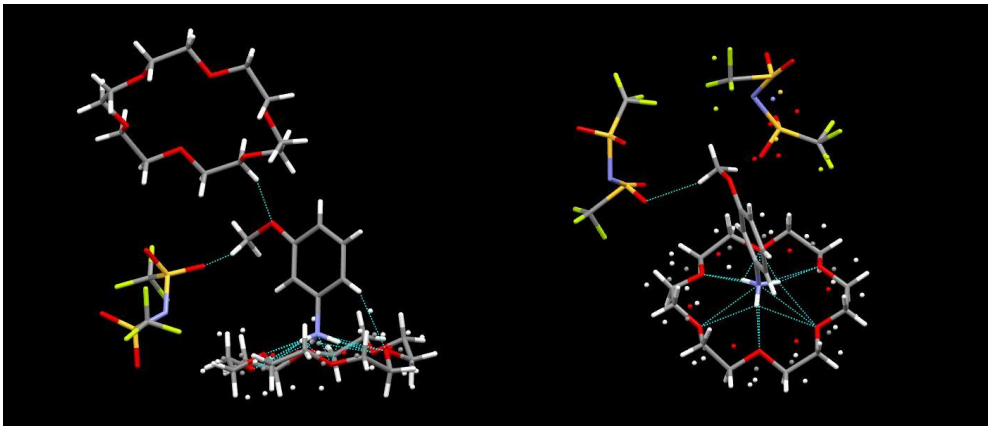

Fig. S11 The short contacts detected between 3-methoxyanilinium cation and surrounding molecules at 293 K (a) and 323 K (b) respectively.

Table. S1 Summary of the crystallographic data for **1** and [(3-methoxyanilinium)(18-crown-6)][PF_6].

Compound	**1**	**1**	[(3-methoxyanilinium)(18-crown-6)][PF_6]
Formula	$C_{21}H_{34}F_6N_2O_{11}S_2$	$C_{21}H_{34}F_6N_2O_{11}S_2$	$C_{19}H_{34}F_6NO_7P$
Formula Weight	668.62	668.62	533.44
Temperature	293 K	323 K	291 K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	11.9353(16)	13.3550(8)	13.3720(2)
b/Å	16.8223(19)	14.4913(6)	13.8419(2)
c/Å	16.703(2)	17.0721(10)	15.1836(3)
a/deg	90	90	90
β/deg	110.336(15)	107.240(7)	116.112(2)
y/deg	90	90	90
Volume/Å^3	3144.5(7)	3155.5(3)	2523.55(8)
Z	4	4	4
Density/g cm^{-3}	1.412	1.407	1.404
R_1 [$I>2\sigma(I)$]	0.0900	0.1327	0.0511
wR_2 [$I>2\sigma(I)$]	0.2785	0.2714	0.1457
GOF	1.012	1.003	1.069

Table. S2 Hydrogen bonds for **1** in LTP and HTP.

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—*H*···*A***
LTP				
N1—H2C···O7	0.89	1.96	2.836(6)	165.6
N1—H2C···O7A	0.89	2.04	2.867(9)	154.6
N1—H2E···O5	0.89	2.01	2.888(6)	167.4
N1—H2E···O5A	0.89	2.02	2.797(12)	145.8
N1—H2E···O6A	0.89	2.20	2.868(11)	131.4
HTP				
N1—H1A···O10	0.89	1.91	2.784(8)	164.8
N1—H1B···O13	0.89	2.20	2.837(18)	128.4
N1—H1C···O8	0.89	1.97	2.848(9)	166.6

Table. S3 Bond lengths [Å] and bond angles [°] for **1** at 293 K.

S1-O1	1.425(3)	O10-C8	1.426(8)
S1-O2	1.429(3)	O7-C3	1.418(7)
S1-N2	1.568(3)	O7-C21	1.397(8)
S1-C1	1.825(5)	O8-C20	1.398(8)
S2-N2	1.573(3)	O8-C12	1.415(8)
S2-O4	1.422(3)	C7-C8	1.514(9)
S2-O3	1.425(3)	C5-C6	1.514(9)
S2-C2	1.819(5)	C9-C10	1.534(9)

O11-C15	1.356(4)	C11-C12	1.477(7)
O11-C19	1.451(5)	C20-C21	1.514(9)
N1-C13	1.468(4)	C3-C4	1.513(8)
F1-C1	1.343(6)	C6A-O5A	1.391(9)
F5-C2	1.317(5)	C6A-C5A	1.534(10)
F6-C2	1.336(6)	C7A-O5A	1.423(10)
F4-C2	1.309(5)	C7A-C8A	1.526(10)
C13-C14	1.395(5)	C5A-O6A	1.422(10)
C13-C18	1.371(5)	O6A-C4A	1.400(9)
C14-C15	1.397(4)	C4A-C3A	1.531(10)
F3-C1	1.315(6)	C3A-O7A	1.416(10)
C15-C16	1.389(5)	O7A-C21A	1.432(9)
F2-C1	1.286(5)	C21A-C20A	1.533(10)
C18-C17	1.388(5)	C1A-O8A	1.393(10)
C16-C17	1.377(5)	O8A-C12A	1.403(9)
O6-C5	1.406(9)	C12-C11A	1.512(10)
O6-C4	1.411(7)	C11-O9A	1.416(10)
O5-C7	1.407(9)	O9A-C10A	1.404(10)
O5-C6	1.430(7)	C10A-C9A	1.526(10)
O9-C11	1.380(8)	C9A-O10A	1.427(10)
O9-C10	1.424(7)	O10-C8A	1.411(10)
O10-C9	1.367(7)		

O1-S1-O2	117.90(19)	F3-C1-F1	107.8(5)
O1-S1-N2	108.54(17)	F2-C1-S1	111.6(4)
O1-S1-C1	103.1(2)	F2-C1-F1	108.3(4)
O2-S1-N2	116.42(17)	F2-C1-F3	107.7(5)
O2-S1-C1	105.1(2)	C21-O7-C3	108.5(7)
N2-S1-C1	103.8(2)	C20-O8-C12	121.0(8)
N2-S2-C2	103.5(2)	O5-C7-C8	106.8(11)
O4-S2-N2	117.01(18)	O6-C5-C6	106.5(10)
O4-S2-O3	118.3(2)	O10-C9-C10	109.6(6)
O4-S2-C2	104.5(2)	O9-C11-C12	109.8(9)
O3-S2-N2	108.02(19)	O5-C6-C5	107.7(11)
O3-S2-C2	103.4(2)	O9-C10-C9	108.4(6)
C15-O11-C19	117.5(3)	O8-C20-C21	116.5(10)
S1-N2-S2	127.0(2)	O7-C3-C4	108.2(7)
C14-C13-N1	118.0(3)	O6-C4-C3	109.9(7)
C18-C13-N1	119.9(3)	O8-C12-C11	113.6(9)
C18-C13-C14	122.1(3)	O7-C21-C20	111.3(9)
C13-C14-C15	118.0(3)	O10-C8-C7	108.0(12)
O11-C15-C14	124.5(3)	O5A-C6A-C5A	101.7(13)
O11-C15-C16	115.5(3)	O5A-C7A-C8A	124(3)
C16-C15-C14	120.1(3)	C6A-O5A-C7A	113.6(16)

C13-C18-C17	119.1(3)	O6A-C5A-C6A	114.9(14)
C17-C16-C15	120.6(3)	C4A-O6A-C5A	108.1(12)
C16-C17-C18	120.2(3)	O6A-C4A-C3A	97.4(14)
C5-O6-C4	111.4(8)	O7A-C3A-C4A	120.7(15)
F5-C2-S2	111.0(3)	C3A-O7A-C21A	126.7(13)
F5-C2-F6	107.4(4)	O7A-C21A-C20A	113.0(18)
F6-C2-S2	112.3(3)	O8A-C20A-C21A	97.1(16)
F4-C2-S2	111.8(3)	C1A-O8A-C12A	106.0(11)
F4-C2-F5	108.4(4)	O8A-C12A-C11A	111.9(16)
F4-C2-F6	105.6(4)	O9A-C11A-C12A	113.1(17)
C7-O5-C6	107.2(8)	C10A-O9A-C11A	102.7(14)
C11-O9-C10	111.5(8)	O9A-C10A-C9A	90.4(16)
C9-O10-C8	109.9(8)	O10A-C9A-C10A	142(2)
F1-C1-S1	110.2(4)	C8A-O10A-C9A	124.2(19)
F3-C1-S1	111.2(3)	O10A-C8A-C7A	91(2)

Table. S4 Bond lengths [Å] and bond angles [°] for **1** at 323 K.

S1-C1	1.890(12)	C20-C21	1.49(2)
S1-N2	1.78(2)	F4-F5A	1.57(4)
S1-O1	1.283(9)	C10-O5	1.413(9)
S1-O2	1.393(9)	C10-C11	1.538(10)
S2-C2	1.679(13)	C14-C15	1.64(3)
S2-O3	1.334(11)	N2-O2	1.82(4)
S2-N2	1.78(2)	C18-C19	1.555(10)
S2-O4	1.291(13)	O5-C21	1.399(9)
N1-C6	1.472(5)	C11-O6	1.426(17)
O17-C4	1.353(6)	C13-C12	1.534(10)
O17-C3	1.409(7)	C12-O6	1.406(9)
C6-C5	1.369(6)	C6A-O16	1.44(3)
C6-C7	1.359(6)	C6A-C00O	1.519(10)
C5-C4	1.384(6)	O16-C00V	1.21(3)
C4-C9	1.374(7)	C00V-C8A	1.48(3)
C7-C8	1.393(7)	C8A-O15	1.35(3)
C8-C9	1.355(7)	O15-C1A	1.15(3)
O7-C14	1.390(9)	C1A-C9A	1.34(3)
O7-C13	1.405(9)	C9A-O14	1.38(3)
O10-C20	1.384(9)	O14-C00Y	1.02(2)
O10-C19	1.418(9)	C00Y-C2A	1.5399(10)
O9-C17	1.416(10)	C2A-O13	1.38(3)
O9-C18	1.408(10)	O13-C00	1.13(3)
C2-F6	1.246(14)	C00-C22	1.48(3)
C2-F5	1.304(16)	C22-O12	1.31(3)
C2-F4	1.362(18)	O12-C4A	1.21(3)
C2-S2A	1.913(15)	C4A-C10A	1.41(3)

C2-F4A	1.36(3)	C10A-O11	1.41(2)
C2-F5A	1.19(2)	O11-C00O	1.404(10)
O8-C16	1.419(10)	N1A-S2A	1.652(11)
O8-C15	1.408(9)	N1A-O1A	1.4198(11)
C1-F1	1.386(12)	N1A-S1A	1.850(14)
C1-F3	1.279(13)	S2A-O1A	1.62(2)
C1-F2	1.213(14)	S2A-O3A	1.356(14)
C1-S1A	2.0993(11)	S2A-O4A	1.379(15)
C1-F3A	1.373(15)	O1A-S1A	1.393(16)
C1-F1A	1.20(2)	O1A-O2A	1.753(18)
C17-C16	1.59(3)	S1A-O2A	1.4198(11)
N2-S1-C1	84.9(10)	O5-C10-C11	103.3(11)
O1-S1-C1	110.5(7)	O7-C14-C15	101.1(12)
O1-S1-N2	164.4(11)	O8-C16-C17	103.4(15)
O1-S1-O2	104.0(8)	S1-N2-S2	106.7(13)
O2-S1-C1	103.2(6)	S1-N2-O2	45.5(8)
O2-S1-N2	68.8(15)	S2-N2-O2	124.6(17)
C2-S2-N2	143.8(11)	O8-C15-C14	108.7(15)
O3-S2-C2	104.4(12)	O9-C18-C19	112.4(13)
O3-S2-N2	105.7(17)	C21-O5-C10	113.7(13)
O4-S2-C2	105.7(9)	O5-C21-C20	108.9(13)
O4-S2-O3	106.3(7)	O6-C11-C10	105.1(12)
O4-S2-N2	84.7(9)	O7-C13-C12	109.4(12)
C4-O17-C3	117.9(5)	O10-C19-C18	108.7(13)
C5-C6-N1	117.9(4)	O6-C12-C13	107.9(11)
C7-C6-N1	119.2(4)	C12-O6-C11	109.2(12)
C7-C6-C5	122.9(4)	O16-C6A-C00O	127(3)
C6-C5-C4	118.5(5)	C00V-O16-C6A	120(2)
O17-C4-C5	124.1(5)	O16-C00V-C8A	110(3)
O17-C4-C9	116.1(6)	O15-C8A-C00V	129(3)
C9-C4-C5	119.8(5)	C1A-O15-C8A	140(3)
C6-C7-C8	117.5(5)	O15-C1A-C9A	113(3)
C9-C8-C7	121.0(5)	C1A-C9A-O14	115(4)
C8-C9-C4	120.4(5)	C00Y-O14-C9A	123(3)
C14-O7-C13	104.8(13)	O14-C00Y-C2A	111(3)
C20-O10-C19	111.3(11)	O13-C2A-C00Y	130(2)
C18-O9-C17	115.4(16)	C00-O13-C2A	113.7(17)
F6-C2-S2	101.1(11)	O13-C00-C22	102(3)
F6-C2-F5	101.0(15)	O12-C22-C00	124(3)
F6-C2-F4	82.7(12)	C4A-O12-C22	130(3)
F6-C2-S2A	128.7(10)	O12-C4A-C10A	115(3)
F6-C2-F4A	132(2)	C4A-C10A-O11	106(2)
F5-C2-S2A	111.5(10)	C00O-O11-C10A	109.1(18)

F5-C2-F4A	95.0(16)	O11-C00O-C6A	91.8(6)
F4-C2-S2	121.8(12)	S2A-N1A-S1A	94.6(7)
F4A-C2-S2A	84.4(15)	O1A-N1A-S2A	63.2(11)
F5A-C2-S2	135.1(16)	O1A-N1A-S1A	48.2(8)
F5A-C2-F6	122.9(17)	N1A-S2A-C2	96.7(7)
F5A-C2-F4	76(2)	O1A-S2A-C2	77.4(8)
C15-O8-C16	102.3(17)	O1A-S2A-N1A	51.4(4)
F1-C1-S1A	101.5(9)	O3A-S2A-C2	105.7(8)
F3-C1-F1	103.5(13)	O3A-S2A-N1A	123.6(8)
F3-C1-S1A	130.6(12)	O3A-S2A-O1A	83.8(10)
F2-C1-S1	113.6(10)	O3A-S2A-O4A	100.3(10)
F2-C1-F1	90.4(12)	O4A-S2A-C2	108.6(15)
F2-C1-F3	135.4(14)	O4A-S2A-N1A	120.5(12)
F2-C1-S1A	85.7(9)	O4A-S2A-O1A	171.2(14)
F2-C1-F3A	81.7(11)	O2A-O1A-S1A	52.1(5)
F2-C1-F1A	123.5(18)	S2A-O3A-O1A	53.8(7)
F3A-C1-S1	98.1(9)	N1A-S1A-C1	84.9(7)
F1A-C1-S1	116.0(15)	O1A-S1A-C1	129.5(10)
F1A-C1-F3A	115.5(17)	O1A-S1A-N1A	49.5(4)
O9-C17-C16	109.6(18)	O1A-S1A-O2A	77.1(10)
O10-C20-C21	110.9(12)	O2A-S1A-C1	86.5(13)
C2-F4-F6	45.7(7)	O2A-S1A-N1A	93.0(13)
C2-F4-F5A	47.2(12)	C1-F3A-F2	45.1(7)
F5A-F4-F6	80.8(14)	O1A-O2A-S1A	50.8(8)